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# Poly(ethylene terephthalate) Modified with Aromatic Bisester Diamides: Thermal and Oxygen Barrier Properties

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**ABSTRACT:** The synthesis and properties of poly(ethylene terephthalate) (PET) copolymers containing four bisester diamide structural units are reported. Two of the bisester diamides consist of three para-substituted aromatic rings, and the other two consist of three meta-substituted aromatic rings. The copolymers have been characterized by nuclear magnetic resonance, differential scanning calorimetry, and dilute solution viscometry. Three of the copolymers can be compression-molded into amorphous films for oxygen barrier testing, and one of these three films can be oriented for additional barrier testing. The three amorphous films all have lower permeabilities than unoriented PET. However, this difference diminishes upon the orientation of the polymer films. © 2004 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 42: 1668–1681, 2004

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## INTRODUCTION

Poly(ethylene terephthalate) (PET) is widely used as a film in packaging applications. PET bottles are lightweight and shatterproof, but the permeation of small gas molecules through PET films prevents their use in certain packaging applications. The permeability coefficient ( $P$ ) of a permeant through a polymer is the product of its diffusion coefficient ( $D$ ) and solubility coefficient ( $S$ ).  $D$ , or the diffusivity, describes the speed of movement of a permeant and, therefore, how easily gas molecules can move from one space to

another in the polymer.  $S$  describes the amount of the permeant that dissolves in the polymer matrix. Thus, the gas permeability of PET might be reduced through the design of copolymers that have less free volume within the polymer matrix or in which the movement of gas molecules through the polymer matrix is impeded. Although  $D$  and  $S$  quantify different physical processes, both values will likely be affected by changes in the polymer structure, and strong correlations between  $D$  and  $S$  have been noted for a family of related partially aromatic copolyesters.<sup>1</sup>

One approach to reducing the permeability of PET is to design comonomers that incorporate rigid linear units into the polyester backbone.<sup>2</sup> When such a copolymer is mechanically oriented, the rigid units aid in the alignment of the polymer chains along the direction of orientation. The

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close packing of the oriented copolymer chains results in a film with less free volume and, therefore, a lower value of  $S$ , than the oriented homopolymer. The closeness of the polymer chains and their increased rigidity should also act to reduce chain motions, thereby lowering the value of  $D$  as well.

Another approach to reducing the permeability of PET is to design comonomers that increase interchain attractive forces through the addition of hydrogen-bonding units to the polyester backbone. For example, ethylene vinyl alcohol copolymers have oxygen permeabilities that are 3–4 orders of magnitude lower than those of polyethylene.<sup>3</sup> Close chain packing in the crystalline phase reduces the free volume available for transport to such an extent that the crystalline phase may be regarded as impermeable with respect to the amorphous phase in most semicrystalline polymers.<sup>4</sup> Because gas diffusion takes place in the amorphous phase, it would be advantageous to design hydrogen-bonding comonomers that do not cocrystallize with PET and, therefore, concentrate in the amorphous domains. Adding hydrogen-bonding units to PET should reduce the segmental motions of the polymer chain, and this should result in a decrease in  $D$  with respect to the homopolymer.

Polyamide (i.e., nylon) analogues of polyesters often have superior thermal and physical properties.<sup>5</sup> The main reason for the difference in the properties comes from the ability of polyamides with primary amides to hydrogen-bond to one another. These strong intermolecular attractions can improve the mechanical strength as well as the chemical and thermal stability. However, these interchain forces have adverse effects on processability. For example, the amide analogue of PET, poly(ethylene terephthalamide) or nylon-(2,T), has a melting temperature ( $T_m$ ) of 455 °C,<sup>6</sup> that of PET is 265 °C.<sup>4</sup> Poly(ester amide) copolymers have been prepared in efforts to combine the mechanical and chemical properties of polyamides with the processability of polyesters.<sup>7–12</sup> One method of preparing poly(ester amide)s is to use bisester diamides as comonomers in a polyesterification. This approach amounts to a standard polyesterification in which the monomer contains two preformed amides. Bisester diamides have been used to prepare alternating poly(ester amide)s<sup>13–17</sup> as well as polyester-type materials with small amounts of randomly distributed diamide units.<sup>18–23</sup>

Gaymans and coworkers<sup>13–16,18,19,21–23</sup> have shown that modifying PET with  $N,N'$ -bis[4(methoxycarbonyl)phenylcarboxy]-1,2-ethanediamine (T2T) improves a number of thermal and mechanical properties. In particular, it is proposed that self-assembly of the amide units through hydrogen bonding leads to an increase in the rate of crystallization from the melt. T2T is the structural equivalent of 1.5 repeat units of PET, in which ethylene glycol has been replaced with 1,2-ethylenediamine. Upon incorporation into PET, the resulting diamide unit is isosteric with the PET repeat unit, and this allows the diamides to fit into the PET lattice. The incorporation of  $N,N'$ -bis[4-(methoxycarbonyl)phenylcarboxy]-1,4-phenylenediamine (T $\Phi$ T), an aromatic bisester diamide that has a poorer fit with the repeat unit of PET, also increases the rate of crystallization, but not as much as T2T.<sup>20–22</sup>

Yamada et al.<sup>24</sup> prepared oligomers of poly(*p*-phenylene terephthalamide) with a degree of polymerization of 4.5. When these oligomers were incorporated into PET, the resulting blocky copolymers showed improved physical properties.<sup>25</sup> Drawn samples of this copolymer show a greater degree of orientation than similarly prepared samples of PET.

Here we describe the synthesis of four bisester diamides used to incorporate aromatic diamide units into PET. These bisester diamides, based on combinations of isophthalic (I) and terephthalic (T) acids with meta (*m*) and para (*p*) isomers of aminobenzoic acid or phenylene diamine, can be divided into two categories: bent aromatic and linear aromatic. The bent aromatic bisester diamides (*mlm* and *ImI*) have been designed to avoid cocrystallization in PET and thus concentrate the hydrogen bonding in amorphous domains. The linear aromatic bisester diamides (*pTp* and *TpT*), which Bouma et al. identified as T $\Phi$ T<sup>22</sup> have been designed as rodlike units to increase polymer orientation in stretched samples.

## EXPERIMENTAL

### Materials

Chloroform was washed with water and dried over  $MgSO_4$  before distillation from  $P_2O_5$ . Dichloromethane was stored over 4-Å molecular sieves before distillation from calcium hydride. All other materials were used as received. All materials were obtained from Aldrich Chemical Co., except

bis(2-hydroxyethyl) terephthalate and mono-methyl terephthalate, which were obtained from KoSa.

#### Characterization

Nuclear magnetic resonance (NMR) spectra were obtained on a Varian Mercury Vx 300-MHz, a Bruker AMX 400-MHz, or a Bruker DMX 500-MHz instrument. Polymer samples were dissolved in a  $\text{CDCl}_3$ /deuterated trifluoroacetic acid (TFA- $d$ ) mixture of about 9:1 (v/v). Infrared characterization was performed with a Nicolet 520 FTIR spectrophotometer.  $T_m$ 's were collected with a Laboratory Devices Melt-Temp II melting-point apparatus. High-resolution mass spectra were obtained on a VG Instruments 70-SE mass spectrometer with electron-impact ionization. Differential scanning calorimetry (DSC) was performed with a PerkinElmer series 7 differential scanning calorimeter. The temperature program provided heating and cooling cycles between 0 and 275 °C at 20 °C/min. Samples were analyzed for the glass-transition temperature ( $T_g$ ) and  $T_m$ . The crystallinity percentage was estimated by a comparison of the measured heat of melting and the theoretical heat of melting for 100% crystalline PET.<sup>26</sup>

Dilute solution viscometry was performed on an AVS 500 viscometer at 25 °C with a 1% polymer solution in dichloroacetic acid. Molecular weights for PET copolymers were approximated with the Mark-Houwink coefficients for PET ( $K = 1.7 \times 10^{-4}$  and  $a = 0.83$ ).

Polymers were dried *in vacuo* at 80 °C for 24 h before the molding. The dry polymers were compression-molded and quenched as amorphous films, as described previously.<sup>27</sup> The temperature of the press was 265 °C, and films were prepared with thicknesses of 180 to 600  $\mu\text{m}$ .

The amorphous films were stretched under constrained uniaxial conditions as described previously.<sup>28</sup> Grids were marked on the film to determine the draw ratio; each specimen was clamped between wide grips and mounted in the environmental chamber of an Instron machine. The films were drawn at  $T_g$  at a rate of 15%  $\text{min}^{-1}$ . After being drawn, each film was cooled rapidly to the ambient temperature in the grips by the door of the environmental chamber being opened.

The density of the polymers was determined with a calcium nitrate/water density gradient column according to ASTM D 1505 Method B. The

column was calibrated with glass floats of known densities. A small piece ( $\sim 25 \text{ mm}^2$ ) of film was placed in the column and allowed to equilibrate for 30 min before the measurement was taken.

Oxygen flux at 23 °C, 0% relative humidity, and 1 atm was measured with a Mocon Ox-Tran 2/20. Films were conditioned as described previously<sup>26</sup> to obtain the non-steady-state oxygen flux, from which  $D$  was determined. The average thickness of each specimen was determined from the measured density after the barrier measurement was completed.<sup>26</sup>

#### *N,N'*-Bis(3-carboxyphenyl)isophthalamide (1)

A solution of isophthaloyl chloride (26.20 g, 128.9 mmol) in 100 mL of  $\text{CHCl}_3$  was added to a mixture of 3-aminobenzoic acid (36.30 g, 264.7 mmol) and triethylamine (37.0 mL, 266 mmol) in 300 mL of  $\text{CHCl}_3$  at 0 °C. The mixture was allowed to warm to room temperature and was stirred for 67 h. The solvent was removed, and the residue was washed with 10% HCl (300 mL). The remaining solid was dissolved in 10% aqueous NaOH (400 mL), and the solution was extracted with diethyl ether ( $2 \times 100 \text{ mL}$ ). The aqueous solution was acidified with 10% HCl (275 mL), and the resulting solid was collected by filtration, washed with 1% HCl (500 mL), and dried under reduced pressure to yield 1 as a pink solid (54.05 g, 104%).

mp: 348–350 °C (decomposed).  $^1\text{H}$  NMR (300 MHz,  $\text{DMSO}-d_6$ ,  $\delta$ ): 10.95 (s, 2H, NH), 8.84 (t,  $J_{\text{meta}} = 2 \text{ Hz}$ , 1H, C2), 8.56 (t,  $J_{\text{meta}} = 2 \text{ Hz}$ , 2H, C2'), 8.19–8.15 (m, 4H, C4', 6'), 7.71–7.67 (m, 3H, C4, 5, 6), 7.49 (t,  $J_{\text{ortho}} = 8 \text{ Hz}$ , 2H, C5'). IR (KBr): 3289 (NH stretching), 1697 (C=O stretching), 1651 (amide I), 1545 (amide II), 1308  $\text{cm}^{-1}$  (C—O stretching).

#### *N,N'*-Bis[3-(methoxycarbonyl)phenyl]isophthalamide (mlm)

1 (25.05 g, 619.5 mmol) was added to a suspension of  $\text{Na}_2\text{CO}_3$  (39.40 g, 371.7 mmol) in 500 mL of dimethylformamide (DMF). The mixture was stirred for 2 h at room temperature under  $\text{N}_2$ . Methyl iodide (9.30 mL, 149 mmol) was added over 1 min. The  $\text{N}_2$  flow was removed, and a drying tube was added. The mixture was stirred for 23 h at room temperature, and this was followed by the addition of 5% HCl (120 mL). The mixture was stirred for another 2 h. The mixture was poured into 1.5 L of  $\text{H}_2\text{O}$  and filtered for the collection of the precipitate. The precipitate was

stirred with an additional 1 L of  $H_2O$ , filtered, and dried under reduced pressure to yield *mIm* as a tan solid (19.62 g, 74%).

mp: 203–207 °C.  $^1H$  NMR (300 MHz,  $CDCl_3$ /TFA-*d*,  $\delta$ ): 8.63 (s, 1H, C2), 8.32 (t,  $J_{meta} = 2$  Hz, 2H, C2'), 8.17 (dd,  $J_{ortho} = 8$  Hz,  $J_{meta} = 2$  Hz, 2H, C4,6), 8.04 (d,  $J_{ortho} = 8$  Hz, 2H, C6'), 7.99 (d,  $J_{ortho} = 8$  Hz, 2H, C4'), 7.76 (t,  $J_{ortho} = 8$  Hz, 1H, C5), 7.59 (t,  $J_{ortho} = 8$  Hz, 2H, C5'), 4.05 (s, 6H,  $CH_3$ ).  $^{13}C$  NMR (300 MHz,  $CDCl_3$ /TFA-*d*,  $\delta$ ): 136.8 (C1'), 134.1 (C1,C3), 131.8 (C4,C6), 130.2 (C5,C3'), 129.9 (C5'), 127.7 (C4'), 127.1 (C2), 127.0 (C6'), 122.9 (C2'). IR (KBr): 3302 (NH stretching), 1723 (C=O stretching), 1651 (amide I), 1545 (amide II), 1295  $cm^{-1}$  (C—O stretching). High-resolution mass spectrometry (electron impact) Calcd. for  $C_{24}H_{20}N_2O_6$ : 432.13214. Found: 432.13176.

### 3-(Methoxycarbonyl)benzoic Acid (2)

A solution of KOH (32.64 g, 0.5817 mol) in 250 mL of  $H_2O$  was added to a solution of dimethyl isophthalate (DMI; 99.99 g, 0.5194 mol) in 150 mL of  $CH_3OH$  at reflux. The mixture was stirred for 40 min and acidified with concentrated HCl (55 mL). The resulting precipitate was collected by filtration. The solid was dried and ground with a mortar and pestle. The powder was triturated with  $CH_2Cl_2$  (500 mL), and this was followed by Soxhlet extraction (10 days) with chloroform.  $CHCl_3$  was removed under reduced pressure to yield 2 as a white solid (23.67 g, 26%). A second Soxhlet extraction (10 days) yielded additional 2 (7.64 g, 8%).

mp: 200–202 °C (lit.<sup>29</sup> 191–192 °C).  $^1H$  NMR (300 MHz, DMSO-*d*<sub>6</sub>,  $\delta$ ): 8.48 (t,  $J_{meta} = 2$  Hz, 1H, C2), 8.20–8.17 (m, 2H, C4,6), 7.67 (t,  $J_{ortho} = 8$  Hz, 1H, C5), 3.88 (s, 3H,  $CH_3$ ). IR (KBr): 1733 (C=O stretching), 1682 (C=O stretching), 1299  $cm^{-1}$  (C—O stretching).

### 3-(Methoxycarbonyl)benzoyl Chloride (3)

The title compound was prepared according to the method of Miyajima et al.<sup>30</sup>  $SOCl_2$  (24.5 mL, 336 mmol) was added to a mixture of 2 (24.04 g, 133.5 mmol) in 125 mL of  $CHCl_3$ . The mixture was heated at reflux for 2 h.  $CHCl_3$  and excess  $SOCl_2$  were removed by distillation under reduced pressure. The residue was recrystallized from petroleum ether to yield 3 as a white solid, which melted upon warming to room temperature (21.53

g, 81%) and which was used without further purification.

mp: 20 °C (lit.<sup>30</sup> 43–45 °C).  $^1H$  NMR (300 MHz,  $CDCl_3$ ,  $\delta$ ): 8.77 (t,  $J_{meta} = 2$  Hz, 1H, C2), 8.37–8.33 (m, 1H, C4), 8.32–8.28 (m, 1H, C6), 7.63 (t,  $J_{ortho} = 8$  Hz, 1H, C5), 3.98 (s, 3H,  $CH_3$ ). IR (neat): 1763 (C=O stretching), 1728 (C=O stretching), 1284  $cm^{-1}$  (C—O stretching).

### *N,N'*-Bis[3-(methoxycarbonyl)phenylcarboxy]-1,3-phenylenediamine (ImI)

A solution of 3 (7.500 g, 377.6 mmol) in 75 mL of  $CHCl_3$  was added to a solution of 1,3-phenylenediamine (1.859 g, 171.9 mmol) and triethylamine (5.8 mL, 42 mmol) in 20 mL of  $CHCl_3$  at 0 °C. The mixture was allowed to warm slowly to room temperature, an additional 40 mL  $CHCl_3$  was added, and the mixture was stirred for 18 h. The reaction mixture was filtered, and the resulting solid was stirred with 5%  $Na_2CO_3$  (50 mL). The solid was collected by filtration, washed with water, and dried under reduced pressure to yield *ImI* as a brown solid (5.817 g, 78%).

mp: 254–256 °C.  $^1H$  NMR (300 MHz,  $CDCl_3$ /TFA-*d*,  $\delta$ ): 8.71 (s, 2H, C2'), 8.35 (d,  $J_{ortho} = 8$  Hz, 2H, C6'), 8.25 (d,  $J_{ortho} = 8$  Hz, 2H, C4'), 8.20 (s, 1H, C2), 7.72 (t,  $J_{ortho} = 8$  Hz, 2H, C5'), 7.60–7.49 (m, 3H, C4', 5', 6'), 4.09 (s, 6H,  $CH_3$ ).  $^{13}C$  NMR (300 MHz,  $CDCl_3$ /TFA-*d*,  $\delta$ ): 137.0 (C1,C3), 134.2 (C4'), 133.6 (C1'), 133.3 (C6'), 130.3 (C5), 129.9 (C3',C5'), 128.5 (C2'), 119.7 (C4,C6), 115.5 (C2). IR (KBr): 3296 (NH stretching), 1729 (C=O stretching), 1650 (amide I), 1545 (amide II), 1257  $cm^{-1}$  (C—O stretching). High-resolution mass spectrometry (electron impact) Calcd. for  $C_{24}H_{20}N_2O_6$ : 432.13214. Found 432.13304.

### Methyl 4-Aminobenzoate (4a)

The title compound was prepared according to the method of Hosangadi and Dave.<sup>31</sup>  $SOCl_2$  (85.0 mL, 1.16 mol) was added over 20 min to methanol (600 mL) in a dry-ice/acetone bath. 4-Aminobenzoic acid (80.00 g, 0.5833 mol) was added quickly, and the stirred mixture was allowed to warm to room temperature. The mixture was stirred for 17 h, and excess methanol was removed by distillation under reduced pressure. Ethyl acetate (200 mL) and 25% aqueous  $Na_2CO_3$  (300 mL) were added to the residue. The resulting two-phase system was mixed well and filtered, and the layers were separated. The ethyl acetate portion was dried over  $MgSO_4$ , and the solvent was removed

on a rotary evaporator to yield **4a** as a tan solid (62.58 g, 71%).

mp: 114–115 °C (lit.<sup>32</sup> 111–112 °C). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, δ): 7.85 (d, *J*<sub>ortho</sub> = 9 Hz, 2H), 6.63 (d, *J*<sub>ortho</sub> = 9 Hz, 2H), 4.02 (s, 2H, NH<sub>2</sub>), 3.85 (s, 3H, CH<sub>3</sub>). IR (KBr): 3469 (NH stretching), 3374 (NH stretching), 1682 (C=O stretching), 1608 (NH bend), 1292 cm<sup>-1</sup> (C—O stretching).

#### Butyl 4-Aminobenzoate (**4b**)

The title compound was prepared according to the method of Hosangadi and Dave.<sup>31</sup> SOCl<sub>2</sub> (15.0 mL, 0.206 mol) was added over 30 min to butanol (200 mL) in a dry-ice/acetone bath. 4-Aminobenzoic acid (18.00 g, 0.1313 mol) was added quickly, and the stirred mixture was allowed to warm slowly to room temperature. The mixture was heated at reflux for 2 h, and excess butanol was removed by distillation under reduced pressure. Ethyl acetate (50 mL) and NaCO<sub>3</sub> (21.84 g dissolved in 75 mL of water) were added to the residue. The resulting two-phase system was mixed well and filtered before the layers were separated. The ethyl acetate layer was dried over MgSO<sub>4</sub>, and the solvent was removed on a rotary evaporator to yield **4b** as a tan solid (12.454 g, 49%).

mp: 59–60 °C (lit.<sup>33</sup> 57 °C). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, δ): 7.85 (d, *J*<sub>ortho</sub> = 7 Hz, 2H), 6.63 (d, *J*<sub>ortho</sub> = 7 Hz, 2H), 4.26 (t, *J* = 7 Hz, 2H, OCH<sub>2</sub>), 4.08 (s, 2H, NH<sub>2</sub>), 1.71 (m, 2H, CH<sub>2</sub>), 1.46 (m, 2H, CH<sub>2</sub>), 0.97 (t, *J* = 8 Hz, 3H, CH<sub>3</sub>). IR (KBr): 3423 (NH stretching), 3346 (NH stretching), 1686 (C=O stretching), 1599 (NH bend), 1281 cm<sup>-1</sup> (C—O stretching).

#### *N,N'*-Bis[4-(methoxycarbonyl)phenyl]terephthalamide (**pTp-a**)

A solution of terephthaloyl chloride (23.97 g, 0.1181 mol) in 200 mL of CHCl<sub>3</sub> was added portionwise to a stirred solution of **4a** (37.50 g, 0.2481 mol) and triethylamine (33.0 mL, 0.237 mol) in 400 mL of CHCl<sub>3</sub> at 0 °C. The mixture was allowed to warm slowly to room temperature and was stirred for 8 h. The solvent was removed on a rotary evaporator, and the residue was dried and ground into a powder. The crude product was triturated with 5% HCl (300 mL), then with 5% NaOH (300 mL), and finally with water (300 mL). The solid was collected by filtration, dried, and recrystallized from *N*-methyl pyrrolidinone. The recrystallized product was triturated twice with

hot acetone and dried under reduced pressure to yield **pTp-a** as a white solid (29.85 g, 58%).

mp: 365–366 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>/TFA-*d*, δ): 8.12 (d, *J*<sub>ortho</sub> = 9 Hz, 4H, C2'), 8.01 (s, 4H, C1), 7.78 (d, *J*<sub>ortho</sub> = 9 Hz, 4H, C1'), 4.03 (s, 6H, CH<sub>3</sub>). IR (KBr): 3329 (NH stretching), 1729 (C=O stretching), 1657 (amide I), 1539 (amide II), 1282 cm<sup>-1</sup> (C—O stretching). High-resolution mass spectrometry (electron impact) Calcd. for C<sub>24</sub>H<sub>20</sub>N<sub>2</sub>O<sub>6</sub>: 432.13214. Found: 432.13142.

#### *N,N'*-Bis[4-(butoxycarbonyl)phenyl]terephthalamide (**pTp-b**)

A solution of terephthaloyl chloride (6.121 g, 30.15 mmol) in 85 mL of CHCl<sub>3</sub> was added portionwise to a stirred solution of **4b** (12.24 g, 63.32 mmol) and triethylamine (8.40 mL, 60.26 mmol) in 75 mL of CHCl<sub>3</sub> at 0 °C. The mixture was allowed to warm slowly to room temperature and was stirred for 23 h. The solvent was removed on a rotary evaporator, and the residue was dried and ground into a powder. The crude product was triturated with 5% HCl (80 mL), then with 5% NaOH (80 mL), and finally with water (80 mL). The solid was collected by filtration, dried, and recrystallized from *N*-methyl pyrrolidinone (ca. 120 g/L, 160 °C). The recrystallized product was triturated twice with hot acetone and dried under reduced pressure to yield **pTp-b** as a white solid (11.97 g, 77%).

mp: 309–311 °C (decomposed). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>/TFA-*d*, δ): 8.11 (d, *J*<sub>ortho</sub> = 9 Hz, 4H, C2'), 8.01 (s, 4H, C1), 7.77 (d, *J*<sub>ortho</sub> = 9 Hz, 4H, C1'), 4.40 (t, *J* = 7 Hz, 4H, OCH<sub>2</sub>), 1.81 (m, 4H, CH<sub>2</sub>), 1.51 (m, 4H, CH<sub>2</sub>), 1.01 (t, *J* = 7 Hz, 6H, CH<sub>3</sub>). IR (KBr): 3368 (NH stretching), 1699 (C=O stretching), 1667 (amide I), 1528 (amide II), 1282 cm<sup>-1</sup> (C—O stretching). High-resolution mass spectrometry (electron impact) Calcd. for C<sub>30</sub>H<sub>32</sub>N<sub>2</sub>O<sub>6</sub>: 516.22604. Found: 516.22580.

#### 4-(Methoxycarbonyl)benzoyl Chloride (**5**)

Excess SOCl<sub>2</sub> (200 mL, 2.74 mol) was added to monomethyl terephthalate (90.09 g, 0.5001 mol), and the mixture was heated at reflux for 19 h. Excess SOCl<sub>2</sub> was removed by distillation under reduced pressure. The residue was recrystallized from hexane to yield **5** as a white solid (86.04 g, 87%).

mp: 57–58 °C (lit.<sup>34</sup> 54–55 °C). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ): 8.18–8.12 (m, 4H), 3.93 (s, 3H).

IR (KBr): 1808 (C=O stretching), 1729  $\text{cm}^{-1}$  (C=O stretching).

*N,N'*-Bis[4-(methoxycarbonyl)phenylcarboxy]-1,4-phenylenediamine (TpT)

A solution of 5 (39.40 g, 0.1984 mol) in 150 mL of  $\text{CHCl}_3$  was added over 20 min to a stirred solution of 1,4-phenylenediamine (8.882 g, 82.13 mmol) and triethylamine (22.90 mL, 164.3 mmol) in 275 mL of  $\text{CHCl}_3$  at 0 °C. The mixture was allowed to warm slowly to room temperature and was stirred for 4 h before heating at reflux for 4 h. The reaction mixture was cooled and filtered, and the solid was dried and ground into a powder. The crude product was triturated with 5%  $\text{NaHCO}_3$  (250 mL), then with 5% HCl (250 mL), and then with water (250 mL). The solid was collected by filtration, dried, and recrystallized from *N*-methyl pyrrolidinone (ca. 20 g/L, 160 °C). The recrystallized product was washed by Soxhlet extraction with  $\text{Et}_2\text{O}$  and dried to yield TpT as a tan solid (21.76 g, 61%).

mp: >400 °C (lit.<sup>35</sup> 371 °C).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3/\text{TFA}-d$ ,  $\delta$ ): 8.19 (d,  $J_{\text{ortho}} = 8$  Hz, 4H, C2'), 7.95 (d,  $J_{\text{ortho}} = 8$  Hz, 4H, C1'), 7.64 (s, 4H, C1), 4.06 (s, 6H,  $\text{CH}_3$ ). IR (KBr): 3342 (NH stretching), 1729 (C=O stretching), 1657 (amide I), 1558 (amide II), 1289  $\text{cm}^{-1}$  (C—O stretching). High-resolution mass spectrometry (electron impact) Calcd. for  $\text{C}_{24}\text{H}_{20}\text{N}_2\text{O}_6$ : 432.13214. Found: 432.13194.

Melt Polymerization

The preparation of a copolyester containing 5% *mIm*, that is, PET-*mIm* (5%), is described here to illustrate the preparation of the copolymers. Bis(2-hydroxyethyl) terephthalate (158.03 g, 621.58 mmol), *N,N'*-bis[3-(methoxycarbonyl)phenyl] isophthalamide (14.141 g, 32.070 mmol), and titanium(IV) *n*-butoxide (221 mg, 649  $\mu\text{mol}$ ) were placed in a glass reaction vessel equipped with a mechanical stirrer, a nitrogen inlet, a distillation head, and a condenser. The mixture was heated under  $\text{N}_2$  for 40 min at 180–200 °C, during which time methanol was removed by distillation. The reaction mixture was heated to 285 °C gradually over a 70-min period. As soon as the temperature reached 285 °C, the pressure was gradually reduced over 15 min to less than 1 mmHg. The reaction mixture was held at 285 °C *in vacuo* for an additional 10 min, during which time ethylene glycol was removed by distillation. The molten

polymer was poured into cold water to quench the reaction. The solid product was vacuum-dried, cryo-ground with dry ice to pass through a 20-gauge mesh, and vacuum-dried again.

Some of the polymers were subjected to solid-state polymerization by the ground polymer being placed in a flask at reduced pressure (<0.2 mmHg). The flask was placed in a heated oil bath (200–230 °C) for 24 h. The temperature of the solid-state polymerization was chosen to be about 30 to 40 °C below  $T_m$  of the polymer.

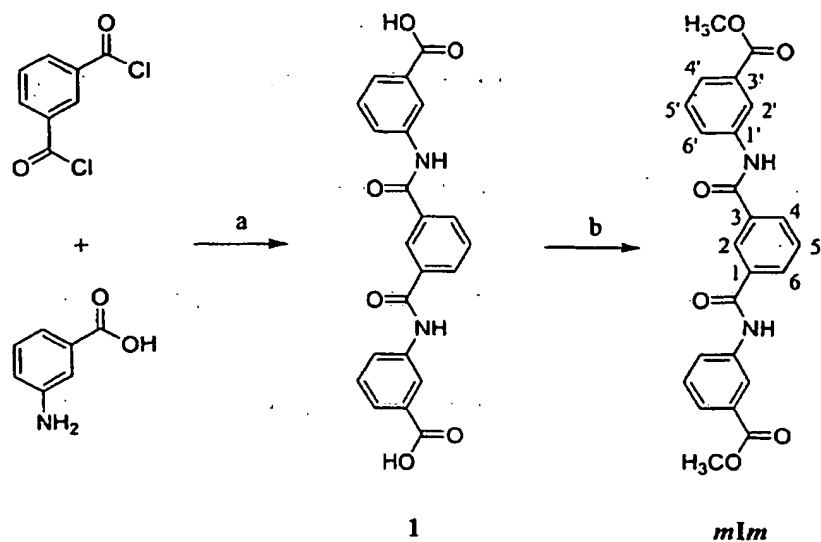
## RESULTS AND DISCUSSION

### Monomer Synthesis

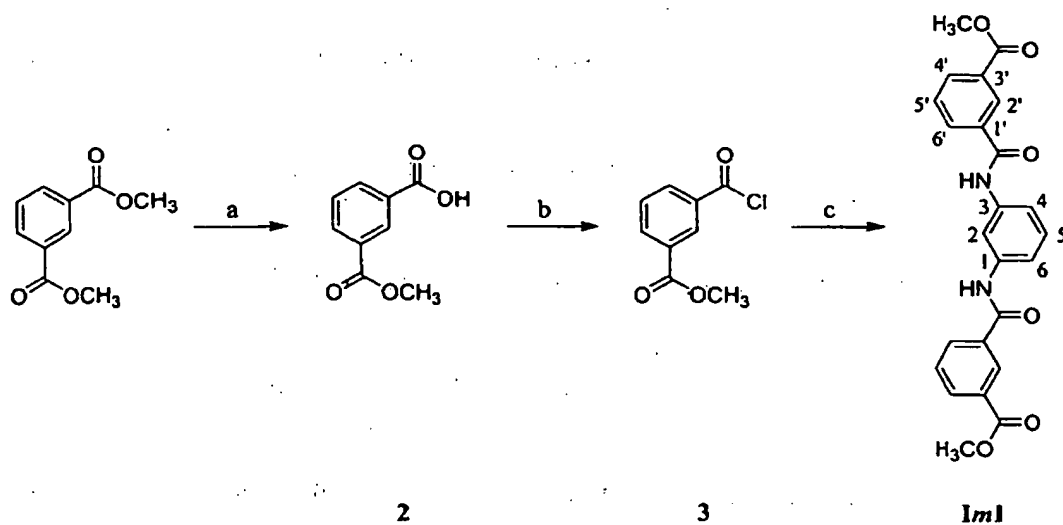
The synthesis of the bisester diamide monomer *mIm* is illustrated in Scheme 1. The reaction of isophthaloyl chloride with excess 1,3-aminobenzoic acid in methylene chloride gave 1 as a precipitate. The diacid 1 is insoluble in methanol, so the preparation of the dimethyl ester *mIm* was performed with methyl iodide in DMF, a method that we previously used to esterify other insoluble diacids.<sup>36</sup>

The synthesis of *ImI* proceeded according to the sequence of reactions shown in Scheme 2. The partial hydrolysis of DMI gave a mixture of unreacted DMI, 2, and isophthalic acid. The desired product 2 was isolated by the washing of the mixture with  $\text{CH}_2\text{Cl}_2$  followed by extraction of the remaining solid with chloroform in a Soxhlet extractor. This process gave higher yields than attempts to prepare 2 by the treatment of isophthaloyl chloride with 1 equiv of methanol followed by the hydrolysis of the remaining acid chloride. The monoacid 2 was converted into the acid chloride 3, which was treated with 1,3-phenylenediamine to afford *ImI*. The complete assignment of the  $^{13}\text{C}$  NMR spectra of *ImI* and *mIm* aided in the determination of the structures of the copolymers. Two-dimensional NMR heteronuclear chemical-shift correlation experiments were used to help assign the peaks in the aromatic regions of the  $^{13}\text{C}$  NMR spectra of *ImI* and *mIm* (see the Experimental section).

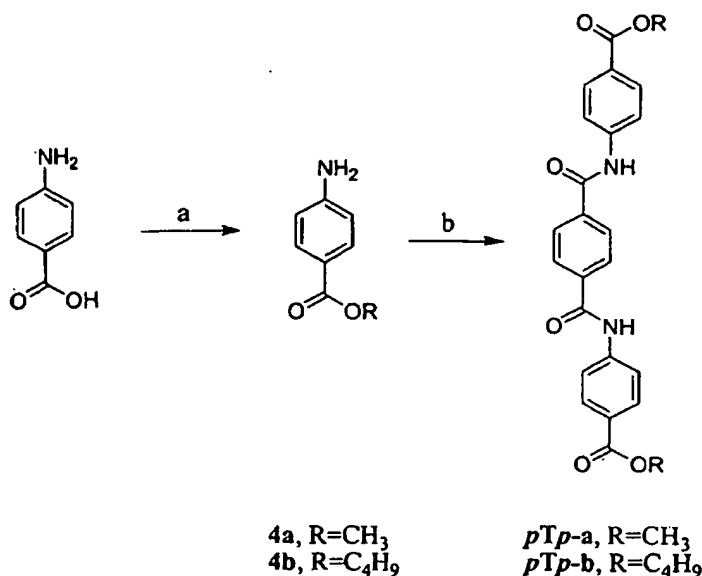
The synthesis of *pTp-a* and *pTp-b* proceeded according to the sequence of reactions shown in Scheme 3. 4-Aminobenzoic acid was converted into its methyl or butyl ester, which was treated with terephthaloyl chloride to afford *pTp*. Mono-methyl terephthalate was converted into the corresponding acid chloride 5, which was treated

(a)  $\text{Et}_3\text{N}$ ,  $\text{CH}_2\text{Cl}_2$ ; (b)  $\text{CH}_3\text{I}$ ,  $\text{Na}_2\text{CO}_3$ , DMF

Scheme 1

(a)  $\text{KOH}$ ,  $\text{H}_2\text{O}$ ,  $\text{CH}_3\text{OH}$ ; (b)  $\text{SOCl}_2$ ; (c) 1,3-phenylenediamine,  $\text{Et}_3\text{N}$ 

Scheme 2



(a)  $SOCl_2$ , ROH; (b) terephthaloyl chloride,  $Et_3N$

Scheme 3

with 1,4-phenylenediamine to afford TpT (Scheme 4).

#### Polymerization

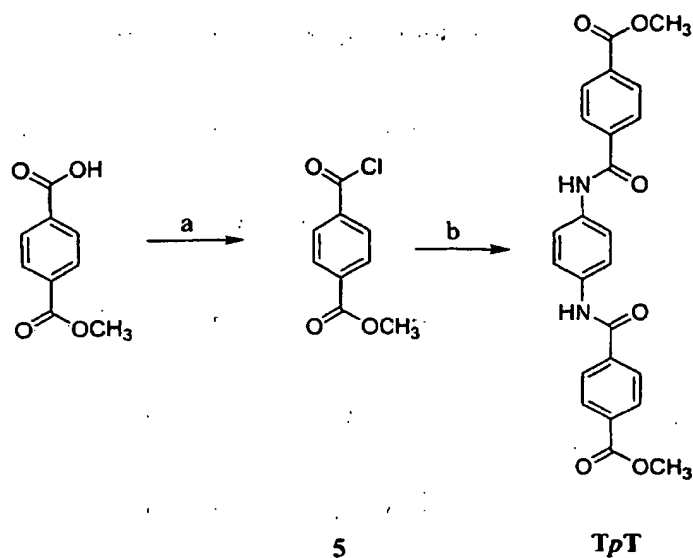
Table 1 summarizes the conditions used to prepare the polymers for this study. The copolymers are named according to the molar ratio of bisester diamide units to terephthalate units. Thus, PET-*mIm* (20%) is PET in which 1 out of every 5 terephthalate units of PET has been replaced with *mIm*.

Many of the polymers were prepared with titanium(IV) *n*-butoxide as a catalyst for both the initial transesterification and the polycondensation steps of the polyesterification. Although this is an efficient catalyst for both steps of the polymerization, some of the polymers prepared in this manner were insoluble in common solvents [e.g., *o*-chlorophenol, dichloroacetic acid, and trifluoroacetic acid (TFA)] after solid-state polymerization. Titanate catalysts have relatively high rate constants for polyester degradation by  $\beta$  elimination, which results in a polymer chain with a terminal vinyl group.<sup>37,38</sup> Bouma and coworkers<sup>15-17</sup> reported that similar poly(ester amide)s

were not completely soluble in 4-chlorophenol after thermal degradation at 320 °C, and they suggested that this was due to crosslinking via terminal vinyl groups. Furthermore, the rate of thermal degradation of poly(ester amide)s was found to be greatly reduced when a zinc/antimony catalyst system was used instead of a titanate.

In an effort to minimize thermal degradation and improve polymer solubility, we prepared other polymers in this study with either zinc acetate or manganese acetate as a transesterification catalyst followed by antimony trioxide as a polycondensation catalyst. All of the polymers prepared with this catalyst system were soluble in solvents suitable for NMR spectroscopy and dilute solution viscometry. The transesterification catalyst ( $ZnOAc_2$  or  $MnOAc_2$ ) was deactivated by the addition of poly(phosphoric acid) before the addition of the polycondensation catalyst ( $Sb_2O_3$ ).

During melt polymerization, the molecular weight is increased by ester interchange reactions with concurrent removal of ethylene glycol by distillation. When bisester diamides are present in molten polyesters, ester-amide interchange reactions can alter the structure of the diamide units.

(a)  $\text{SOCl}_2$ ; (b) *p*-phenylene diamine,  $\text{Et}_3\text{N}$ 

Scheme 4

If the bisester diamide is based on a central diacid unit with two adjacent amines, such as *mIm* and *pTp*, ester-amide interchange reactions will disrupt the diamide units and result in polymers with single, isolated amides. To minimize the possibility of disrupting the diamide units, we stopped melt polymerizations with *mIm* and *pTp* after 25–40 min at 285 °C. The polymers were

then solid-state-polymerized at 200–230 °C. Those copolymers with low  $T_m$ 's after the melt polymerization were not subjected to a solid-state polymerization step.

If the bisester diamide is based on a central diamine unit, such as *ImI* and *TpT*, ester-amide interchange reactions can result in polymer chains with blocks of more than two adjacent

Table 1. Results of the Synthesis of the Copolymers<sup>a</sup>

Monomer	Monomer Charged (mol %)	Monomer Incorporated (mol %)	Catalyst (mol %)	Time at 285 °C (min)	$M_v^b$ before SSP <sup>c</sup> (g/mol)	SSP Temperature (°C)	$M_v$ after SSP (g/mol)
None	0	0	Zn/Sb (0.05/0.05)	30	3,900	229	11,700
<i>mIm</i>	5	5	Ti (0.10)	25	5800	202	10,200
<i>mIm</i>	20	19	Ti (0.10)	25	5,100	—	—
<i>ImI</i>	5	4	Ti (0.11)	25	5800	204	10,600
<i>ImI</i>	20	20	Zn/Sb (0.05/0.05)	25	4,700	—	—
<i>pTp-a</i>	4	2	Ti (0.10)	45	7,400	202	11,600
<i>TpT</i>	4	3	Mn/Sb (0.03/0.03)	140	15,400	—	—

<sup>a</sup> Mn = Mn(OAc)<sub>2</sub>; Sb = Sb<sub>2</sub>O<sub>3</sub>; Ti = Ti(OC<sub>4</sub>H<sub>9</sub>)<sub>4</sub>; Zn = Zn(OAc)<sub>2</sub>.

<sup>b</sup>  $M_v$  = molecular weight determined by dilute solution viscometry.

<sup>c</sup> SSP = solid-state polymerization.

amides. Using  $^{13}\text{C}$  NMR, Serrano and coworkers<sup>7-12</sup> were able to quantify the amide block segments that formed as a result of ester-amide interchange reactions in the synthesis of perfectly alternating poly(ester amide)s from a bisester diamide and a diol. Complete randomization of a molten alternating poly(ester amide) can take several hours, and the formation of amide blocks can be controlled by the minimization of the time for which the polymer is at high temperatures.<sup>18</sup> Bouma et al.<sup>15-17</sup> prepared copolymers of bisester diamides in PET with no detectable large amide segments with a short melt polymerization followed by a solid-state postcondensation.

Bisester diamide monomer TpT is based on a central diamine with terephthalate-type units attached to either end, so ester-amide interchange reactions in a PET polymerization will only affect amide block lengths and not the structure of the TpT triad bisester diamide unit. Because the copolymers with TpT contain only 4 mol % of this comonomer, the formation of large amide blocks is statistically unlikely. Accordingly, the melt polymerization with TpT was allowed to run for 140 min at a high temperature (285 °C). The resulting copolymer had a high enough molecular weight (15,400 g/mol) that a solid-state polymerization step was not necessary. Like TpT, ImI is based on a central diamine, but because the two adjacent diacid units are meta-substituted, ester-amide interchange reactions can disrupt the structure of the monomer by replacing an isophthalate unit with a terephthalate unit. Accordingly, melt polymerizations with ImI were run under the same conditions as polymerizations with mIm and pTp.

The two bent monomers, mIm and ImI, were incorporated into PET at levels of up to 20 mol %. The molten reaction mixtures containing these monomers were clear and homogeneous throughout the polymerization. The synthesis of higher compositions was not attempted.

The two linear monomers containing methyl esters, pTp-a and TpT, were each incorporated into PET at only the 4 mol % level. The molten reaction mixtures containing either of these monomers were opaque until the temperature was raised to approximately 260 °C, at which point they became clear and homogeneous. Attempts to incorporate either of these two monomers into PET above the 4 mol % level resulted in reaction mixtures that were opaque throughout the polymerization.  $^1\text{H}$  NMR analysis of these reaction products showed methyl ester peaks due to bisester diamides that had not undergone

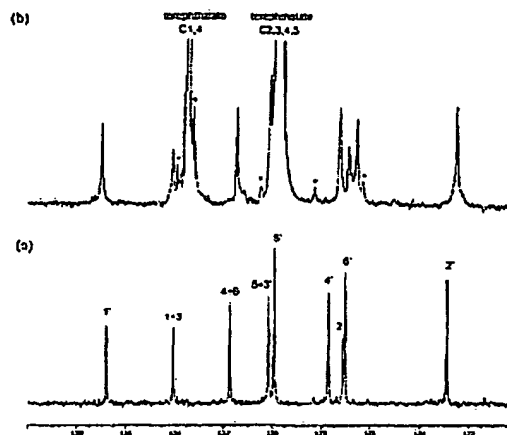


Figure 1.  $^{13}\text{C}$  NMR spectra of (a) mIm and (b) PET-mIm (20%). Peaks that are presumed to come from the products of ester-amide interchange reactions (i.e., peaks that do not correspond to carbon atoms in terephthalate or diamide units) are marked with an asterisk.

transesterification during the polymerization. The long, rigid nature of pTp-a and TpT probably limit their solubilities in the PET reaction mixtures (they are also insoluble in DMSO, unlike the other three bisester diamide monomers in this study). To improve the solubility of pTp-a, we prepared the dibutyl ester analogue pTp-b. However, PET copolymerizations with greater than 4 mol % pTp-b produced materials similar to those made with greater than 4 mol % of the methyl ester, pTp-a.

#### Structural Characterization

$^{13}\text{C}$  NMR spectroscopy was used to detect ester-amide interchange reactions occurring during polymerization. The aromatic region of the spectrum of mIm has 10 peaks (Fig. 1). In the spectrum of PET-mIm (10%), seven of the peaks due to incorporated diamide units are clearly visible. The remaining three peaks are obscured by the peaks for the carbon atoms of the terephthalate units. The spectrum has some peaks that do not correspond to peaks in the spectrum of comonomer mIm. Although these may arise from products of ester-amide interchange, they are relatively small, and this indicates that the majority of mIm survived the polymerization intact.

A similar analysis of PET-ImI (20%) shows that five of the peaks due to incorporated diamide

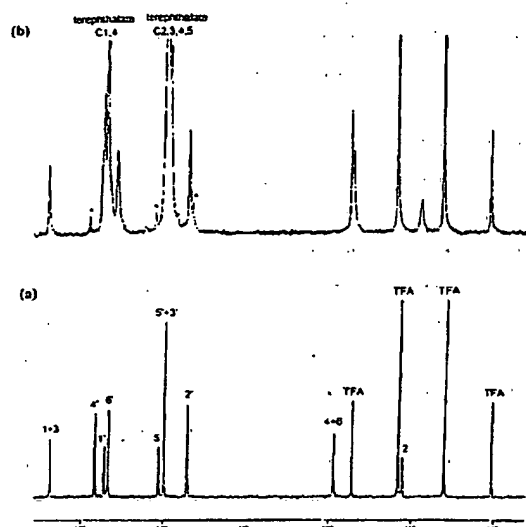


Figure 2.  $^{13}\text{C}$  NMR spectra of (a) ImI and (b) PET-ImI (20%). Peaks that are presumed to come from the products of ester-amide interchange reactions (i.e., peaks that do not correspond to carbon atoms in terephthalate or diamide units) are marked with an asterisk.

units are visible, with the remaining five peaks obscured by the terephthalate carbon peaks (Fig. 2). Here again, the spectrum of the copolymer has some additional small peaks that may arise from ester-amide interchange products (most notably, the peaks at 134.6, 130.5, and 128.2 ppm are due to isophthalate diester moieties), but the majority of ImI is structurally intact.

The compositions of the copolymers were determined by the integration of the peaks in the  $^1\text{H}$  NMR spectra corresponding to the structural

units derived from the bisester diamides. PET-*mIm* copolymers had many overlapping peaks in the NMR spectra, so the well-resolved signal for the protons meta to the esters in the bisester diamide ( $\delta = 7.55$  ppm) was used to quantify the amount of *mIm* incorporated. Likewise, PET-*ImI* copolymers had many overlapping peaks in the NMR spectra, so the well-resolved signal for the protons attached to C2' in ImI ( $\delta = 8.62$  ppm) was used to quantify the amount of ImI incorporated. The NMR spectrum of PET-*pTp* had a singlet for the terephthalamide protons ( $\delta = 8.01$  ppm) that was used to quantify the amount of *pTp* incorporated. The NMR spectrum of PET-*TpT* had a singlet for the protons of the *p*-phenylene diamine unit ( $\delta = 7.64$  ppm) that was used to quantify the amount of *TpT* incorporated.

#### Thermal Analysis

The results of the thermal analysis of the polymers are given in Table 2. The addition of any of the bisester diamide monomers leads to an increase in  $T_g$ . This might arise from hydrogen bonding or increased rigidity of the polymer backbone, which suppress segmental motion. It has previously been shown that a PET copolymer with 6 mol % hydroquinone (HQ) has a  $T_g$  that is only 2 °C higher than that of PET.<sup>39</sup> The incorporation of HQ into PET creates a repeat unit that is similar in shape and flexibility to a *TpT* unit, but the HQ copolymer cannot form hydrogen bonds. Because PET-*TpT* (4%) has a  $T_g$  that is 11 °C higher than that of PET, the increase in  $T_g$  must largely be due to hydrogen bonds formed by the *TpT* units. It has also previously been shown that a PET copolymer with 20 mol % *p*-aminobenzoic acid (PABA) has a  $T_g$  that is 23 °C higher

Table 2. Results of the Thermal Analysis of the Copolymers

Polymer	$T_g$ (°C)	$\Delta C_p$ (J/g°C)	$T_m$ (°C)	$\Delta H_m$ (J/g)	Crystallinity (%)	$T_c$ (°C)	$T_m - T_c$ (°C)
PET	80	0.112	255	43	31	202	53
PET- <i>mIm</i> (5%)	85	0.127	237	32	23	185	52
PET- <i>mIm</i> (19%)	90	0.316	—	—	0	—	—
PET- <i>ImI</i> (4%)	88	0.159	237	33	23	178	59
PET- <i>ImI</i> (20%)	90	0.263	201	14	10	150	51
PET- <i>pTp</i> -a(2%)	86	0.129	243	34	24	180	63
PET- <i>TpT</i> (3%)	85	0.305	245	34	24	166	79

$\Delta C_p$ : change in heat capacity.

$\Delta H_m$ : enthalpy of melting.

Table 3. Oxygen Barrier Results for the PET Copolymers

Polymer	Density (g/cm <sup>3</sup> )	$P$ [cc(STP)cm/m <sup>2</sup> /atm/day]	$D$ (10 <sup>-13</sup> m <sup>2</sup> /s)	$S$ [cc(STP)/cm <sup>3</sup> /atm]
PET	1.3370 ± 0.0004	0.458 ± 0.004	5.2 ± 0.1	0.102 ± 0.002
PET- <i>mIm</i> (5%)	1.3377 ± 0.0001	0.342 ± 0.003	4.9 ± 0.1	0.080 ± 0.002
PET- <i>ImI</i> (5%)	1.3380 ± 0.0004	0.351 ± 0.006	4.4 ± 0.1	0.093 ± 0.003
PET- <i>TpT</i> (4%)	1.3388 ± 0.0005	0.352 ± 0.001	4.3 ± 0.0	0.094 ± 0.001
PET (Oriented, $\lambda = 4.0$ )	1.3537 ± 0.0010	0.203 ± 0.001	3.7 ± 0.1	0.063 ± 0.001
PET- <i>TpT</i> (4%) (Oriented, $\lambda = 4.0$ )	1.3485 ± 0.0004	0.203 ± 0.003	3.5 ± 0.1	0.066 ± 0.003

than that of PET, whereas a PET copolymer with 20 mol % *p*-hydroxybenzoic acid (PHBA) has a  $T_g$  that is 1 °C lower than that of PET.<sup>12</sup> Because PABA and PHBA units have similar shapes and flexibilities, it is apparent that the ability of the PABA unit to hydrogen-bond is responsible for the increase in  $T_g$ .

The addition of any of the bisester diamides leads to a decrease in  $T_m$ , as one would expect when a small amount of a comonomer is added to a homopolymer. The heats of melting of all the copolymers are lower than that of PET, so the incorporation of diamide units has led to copolymers that are less crystalline than PET. Despite their relatively low molecular weights, the two copolymers with relatively high amounts of bisester diamide, PET-*mIm* (20%) and PET-*ImI* (20%), are less crystalline than the other copolymers listed in Table 2. PET-*mIm* (20%) is amorphous and does not have a crystallization peak or a melting peak in the DSC thermogram. PET-*ImI* (20%) shows a small melting peak in the DSC thermogram.

All of the copolymers in Table 2 with diamide units incorporated at low levels (i.e., 2–5%) are 23–24% crystalline. However, the bent and linear diamide units have different effects on the extent of supercooling of the melt phase ( $T_m - T_c$ , where  $T_c$  is the crystallization temperature). Copolymers with low levels of bent diamides supercool similarly to PET, whereas copolymers with low levels of linear diamides supercool noticeably more than PET. The incorporation of higher levels of diamide units (19–20%) results in copolymers with drastically reduced crystallinities, even though PET-*ImI* (20%) supercools 2 °C less than PET. The high supercooling value for PET-*TpT* (3%) is in contrast to an earlier report that PET with 2% of the same diamide unit has a supercooling value that is 10 °C below that of PET.<sup>20–22</sup>

### Oxygen Barrier

The determination of the barrier properties of poly(ester-co-amides) was limited to samples that could be compression-molded to afford high-quality amorphous films. Oxygen barrier results for those copolymers that could be tested are given in Table 3. To avoid measuring differences in barrier properties arising from different levels of crystallinity, we performed all measurements on quenched (amorphous) films of the three copolymers prepared as described previously. The humidity, which strongly affects the barrier properties of polyamides, was held at 0%. Bouma et al.<sup>23</sup> reported that poly(ester amide)s containing 25 mol % T2T absorbed amounts of water similar to that absorbed by the PET homopolymer. Because the  $T_g$  values of samples reported here are not dramatically depressed with respect to PET, we infer that any differences in the water uptake have only a minimal influence on the transport properties. PET-*pTp* and the PET homopolymer (Tables 1 and 2) were too brittle to be compression-molded into films, so no gas barrier data were obtained for them. The PET control sample in Table 3 was commercial-grade PET with a molecular weight of about 20,000 g/mol. All of the films, except for PET-*TpT* (4%), were too brittle to stretch, so barrier experiments on oriented films were limited to that one case.

The incorporation of *mIm*, *ImI*, or *TpT* at 4–5 mol % reduces the permeability of PET by about 25%. Interestingly, both of the bent bisester diamides (*mIm* and *ImI*) and the linear bisester diamide (*TpT*) have similar effects on  $P$ . The change in  $P$  is due to decreases in both  $D$  and  $S$ . The decrease in  $D$  arises from reduced chain mobility due to the introduction of hydrogen bonding in much the same fashion as hydrogen bonding accounts for the very low oxygen diffusivity of polyamides.<sup>4,40</sup> The substantial decrease in  $D$  pro-

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